PB87-130274

Report for Non-Flame Hazardous Waste Thermal Destruction

(U.S.) Environmental Protection Agency
Cincinnati, OH

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-130274

EPA/600/2-86/105
December 1986

Report for Non-Flame Hazardous Waste Thermal Destruction

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Work Plan 01206
Item 3435[L]

Office of Research and Development
Office of Environmental Engineering and Technology
Hazardous Waste Engineering Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/2-86/105		PB87 130274/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
REPORT FOR NON-FLAME HAZARDOUS WASTE THERMAL DESTRUCTION	December 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Myron Malanchuk	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
U.S. Environmental Protection Agency Hazardous Waste Engineering Research Laboratory Cincinnati, OH 45268	11. CONTRACT/GRANT NO. In-house
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U.S. Environmental Protection Agency Hazardous Waste Engineering Research Laboratory Cincinnati, OH 45268	Final 1/85 - 7/86 14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A laboratory apparatus, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system, has been used to investigate the impact of key factors of the post-flame zone in the combustion process upon the effluent decomposition products. The results from thermal treatment of various organic compounds showed that:

(1) Very good reproducibility under similar test conditions was obtained for effluent composition/concentration from initial thermal treatment tests, of a solid, pentachloronitrobenzene, and a volatile organic, chloroform.

(2) Thermal decomposition profiles of individual organic compounds introduced as the feed material to the system provided DE (Destruction Efficiency) values for each compound.

(3) Products of Incomplete Combustion (PICs) were generated, sometimes in major quantity, that accounted for a large portion of the elemental composition of the feed material.

(4) Test series concentrating on the thermal treatment of chloroform showed major differences in PIC generation as a result of different atmospheres (rich oxygen and reduced oxygen). It appeared that several hundred degrees (°C) higher temperature would be needed to attain the same degree of destruction of the more refractory PICs in the reduced oxygen atmosphere as was shown in the rich oxygen case.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	Unclassified	45
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report describes the results of experimentation in non-flame hazardous waste thermal destruction carried out at EPA's Center Hill Facility in Cincinnati, Ohio.

For further information, please contact the Alternative Technologies Division/Thermal Destruction Branch of the Hazardous Waste Engineering Research Laboratory.

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Report on Non-Flame Hazardous Waste Thermal Destruction

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ABSTRACT

A laboratory apparatus, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system, has been used to investigate the impact of key factors of the post-flame zone in the combustion process upon the effluent decomposition products. The results from thermal treatment of various organic compounds have been used to:

1. Establish the reproducibility of similar test conditions.

2. Plot the thermal decomposition profiles of the feed material (Principal Organic Hazardous Constituent [POHC]) and the formation/decomposition profiles of the thermal products (Products of Incomplete Combustion [PICs]).

3. Determine the temperatures required to achieve designated levels of Destruction Efficiency (DE) of the POHC.

4. Evaluate the differences in product emissions (effluent composition) with changes in atmosphere types (rich oxygen and reduced oxygen) in the thermal reactor.

5. Indicate the impact of PIC formation.

The preliminary runs in the study confirmed very good reproducibility of results obtained under controlled conditions.

Subsequent runs made on various feeds at different thermal exposure conditions revealed a multiplicity of PICs formed in some cases. Indications were that in industrial incineration systems similar treatment of chlorinated organic compounds could generate PICs at concentration levels having potentially high environmental significance.

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ABBREVIATIONS/SYMBOLS in the REPORT

DE - Destruction Efficiency
DRE - Destruction and Removal Efficiency
ϕ - Ratio of stoichiometric oxygen requirement to the actual oxygen available for reaction with the organic compound, to form CO_2 and H_2O
FID - Flame Ionization Detector
GC - Gas Chromatograph
GC-MS - Gas Chromatograph-Mass Spectrometer
MSD - Mass Selective Detector
PIC - Product of Incomplete Combustion
POHC - Principal Organic Hazardous Constituent
TDAS - Thermal Decomposition Analytical System
TDU-GC - Thermal Decomposition Unit-Gas Chromatograph
UDRI - University of Dayton Research Institute

REPORT ON NON-FLAME HAZARDOUS WASTE THERMAL DESTRUCTION

INTRODUCTION

In the thermal destruction of hazardous organic waste material, the interactions of the gaseous/vapor components in the post-flame or the non-flame zone of the incineration system may have a significant effect upon the composition of the final emissions leaving the stack. The thermal decomposition in those zones can range from simple pyrolysis in an oxygen-deficient atmosphere as might occur in a boiler plant or incinerator, to a thermal-oxidative environment with a considerable excess of oxygen as can occur for example in a liquid injection incinerator supported by a secondary combustion zone or secondary supply of air.

The incinerator is required by RCRA regulations to accomplish no less than a 99.99 percent Destruction and Removal Efficiency (DRE) of the Principal Organic Hazardous Constituents (POHCs) in the waste feed. If the POHC, upon passing through the flame zone is not destroyed to the 99.99% level, then the remainder of it must undergo sufficient destruction (plus removal) in the post-flame zone to achieve the required 99.99% reduction. A combination of moderately high temperature (e.g., 800°C) and extended residence time (e.g., 2.0 seconds) may promote additional decomposition of the POHC substance in the non-flame zone that is sufficient to provide an overall destruction efficiency greater than the required 99.99%.

A laboratory unit, identified as the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC), was used to investigate key thermal decomposition factors of the post-flame zone, such as temperature and oxygen/waste-compound ratio, and their impact upon the effluent decomposition products. The TDU-GC was developed at the University of Dayton Research Institute (UDRI) and has been applied by Institute personnel, along with its companion equipment, the Thermal Decomposition Analytical System (TDAS), to study many different organic compounds over the past several years (1-6).

The TDU-GC at EPA's Center Hill Facility has been used to develop data that supplemented the findings by UDRI for organic compounds treated under like thermal reaction conditions. The initial series of runs were made on such compounds as the non-volatile pentachloronitrobenzene (PCNB) and the volatile chloroform ($CHCl_3$) in order to determine the level of reproducibility, as measured by the comparison of the results to those reported by the UDRI for the same compounds under the same test conditions. Ensuing series investigated compounds in greater depth (e.g., over a wider temperature range) and under different test conditions (e.g., different carrier

gas during the thermal reactor run). Much effort was devoted to the study of chloroform which proved to generate a considerable multitude of Products of Incomplete Combustion (PICs), some of which were quite refractory in comparison with the POHC (feed) material.

EXPERIMENTAL PROCEDURE

A. APPARATUS

The principal equipment used in this study was the Thermal Decomposition Unit-Gas Chromatograph, described in detail in a University of Dayton Research Institute report (1).

A summary of its construction and operation follows.

The TDU-GC system consists of two basic units: (1) the thermal reactor, for exposing the organic component(s) in the feed to an elevated temperature; (2) the analyzer, consisting of a gas chromatograph for separating the components in the effluent sample drawn directly from the reactor. These units are readily identified in the basic schematic system, Figure 1, along with some of the accessory equipment.

1. The thermal reactor incorporates a capillary quartz tube within a furnace with three heating zones that are independently controlled to produce temperatures up to 1150°C in the central zone.

A tubular quartz extension at the entrance of the furnace transfers the feed gas from the larger bore sample insertion chamber. That chamber is fitted with any one of several probes adapted to handle gas, liquid, or solid samples. The liquid and solid samples are converted to vapors at elevated temperatures provided by a heating jacket. The vapor is conveyed to the reactor by a controlled flow of carrier gas; that gas is selected according to the nature of the atmosphere required in the high-temperature zone of the reactor. Compressed air was used to supply a highly oxidative atmosphere; nitrogen or helium was used to provide a pyrolytic or near-pyrolytic atmosphere. According to the temperature and pressure measured in the reactor tube, the carrier gas flow is regulated at the instrument console to provide a precise residence time of the vapor/gas sample in the closely-controlled high-temperature zone.

The gaseous emissions from the reactor pass through a capillary tube into an in-line tubular trap controlled to sub-ambient temperatures usually as low as -50°C, and sometimes even colder. The trap is located inside the wall of the gas chromatograph (GC) and is a very short (several mm) section of the extension of the GC capillary column into the 30:1 splitter device.

2. The gas chromatograph, Varian model 3700, is fitted with a fused silica capillary column leading to a flame ionization detector (FID). Heating the trap transfers, via the 30:1 splitter, the smaller stream of trapped emissions sample to the front end of the capillary column, which itself is at the sub-ambient temperature. Upon injection of the sample into the GC, as initiated by the switch on the CDS-111 computer, the

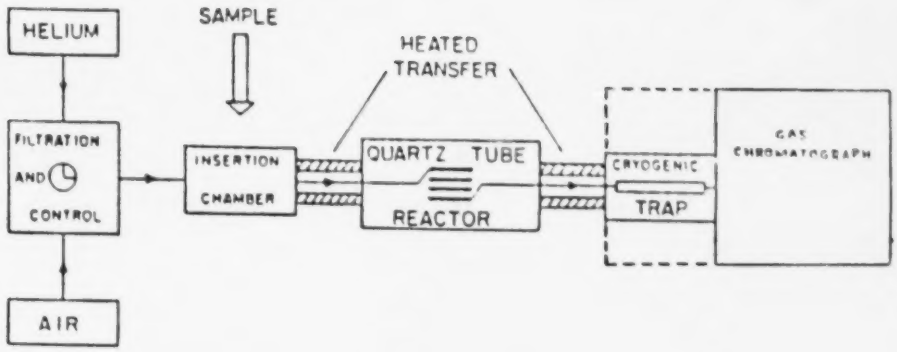

Figure 1. Basic Schematic of TDU-GC System

temperature program for the capillary column controls the separation of the components of the reactor emissions sample and their ensuing detection and measurement by the FID.

The CDS-111 computer coupled with an Omniscribe recorder provides a means of storing the output of the FID and depicting it in a chromatogram of component peaks on the recorder as well as in a tabulation/measurement of each peak area on the computer tapes.

3. Other equipment, critical to the various measurements involved in the operation of the TDU-GC system, include:

a. Syringes, of various volumes and types
b. Soap bubble flowmeter and stopwatch
c. Aneroid barometer
d. Room temperature thermometer
e. Vapor concentration flask, for preparing known gaseous concentrations of volatile organic compounds.
f. Calculator, for determining the flow rate of carrier gas during the thermal reaction run, from the temperature and pressure measurements around and in the TDU-GC system.

B. REAGENTS and SUPPLIES

1. The many compounds tested were reagent grade material obtained from a commercial supplier or from a quality control laboratory. They included:

a. Pentachloronitrobenzene (PCNB), $C_6Cl_5NO_2$ (QA5/EMSL, EPA/RTP)
b. Chloroform, $CHCl_3$ (HPLC Grade/Fisher Scientific C-606)
c. Heptane, C_7H_{16} (Distilled in glass/Burdick and Jackson AA-167)
d. Monochlorobenzene, C_6H_5Cl (Certified Grade/Fisher B-255)
e. Carbon tetrachloride, CCl_4 Analytical Reagent/Mallinckrodt 4368)
f. Trichloroethylene, C_2HCl_3 (Certified ACS/Fisher T-341)
g. Freon-113, $C_2Cl_3F_3$ (Reagent Grade/Fisher T-180)

2. In addition, the various organic compounds used in a calibration procedure to confirm GC retention time identities included:

a. Dichloroethane, $C_2H_4Cl_2$ (Certified ACS/Fisher E-175)
b. Tetrachloroethylene, C_2Cl_4 (Reagent/Baker 9465-1)
c. Hexachloroethane, C_2Cl_6 (Kodak 144)
d. Pentachloroethane, C_2HCl_5 (min. 96% purity/Ultra Scientific RHH-18)
e. Hexachlorobenzene, C_6Cl_6 (Ultra Scientific CH-150)
f. Methylene chloride, CH_2Cl_2 (Distilled in glass/Burdick and Jackson)
g. Heptane, C_7H_{16} (Sequenation grade/Kodak 13068)
h. Heptane, C_7H_{16} (>99.7% purity/Fluka CH9470)
i. Methanol, CH_3OH (Certified grade/Fisher A-936)

3. Cylinder gases for the transfer of the test gas/vapor through the reactor and/or the GC and for the operation of the FID were:

a. Compressed air (Hydrocarbon free/Linde)
b. Helium (High purity/U.S. BuMines)
c. Hydrogen (Zero grade/Matheson)
d. Nitrogen (Zero grade/Linde)

The gas transfer lines from the nitrogen and the helium supply cylinders were provided with gas purifier columns to remove oxygen and water in the gas supplied to the reactor and the GC.

C. SAMPLE FEED

The POHC material under investigation was introduced into the insertion chamber as a (1) gas, (2) liquid, or (3) solid.

1. The more volatile, low molecular weight compounds were generally fed to the TDU-GC system in vapor form. For example, a calculated amount of liquid chloroform was delivered from a syringe into a closed 1-liter flask containing air at atmospheric pressure to produce a concentration of 1.00 μg chloroform per 10 μl of the flask air. Then an appropriate quantity of that vapor preparation (10-100 μl) was drawn into a syringe for injection into the TDU-GC insertion chamber.

2. For various organic liquids, nanoliter quantities (10-100 nl) were injected directly into the insertion chamber and vaporized according to a programmed increase of temperature for transfer by the carrier gas into the thermal reactor.

3. Organic solids were weighed out on a microbalance and then dissolved in such solvents as cyclohexane or methanol to produce the required concentrations. An aliquot, perhaps 1-10 μl of the solution, was drawn into a syringe and then carefully injected onto the end of the "solids probe". Evaporation of the solvent left a residue of the organic solid on the tip of the probe which was then expeditiously fitted to the insertion chamber. A programmed temperature elevation of the chamber transformed the solid residue to the vapor state for transfer into the thermal reactor by the carrier gas.

D. TEST RUN

The procedure for a test run is fully described in the UDRI report (1).

Initially, the parameters of atmosphere type, temperature level in the thermal reactor and mean residence time were selected and the necessary steps taken to set those conditions. The temperature selected was adjusted by the controls on the furnace. A source of the required carrier gas was regulated by the instrumentation console control (valve switch and flow control) to provide the necessary flow rate for maintaining the selected residence time of the test gas sample in the high-temperature zone of the furnace. The effluent collection trap in the wall of the GC was cooled to

the sub-ambient temperature selected as the starting point for the GC analysis program. The sample was then introduced into the insertion chamber where it was vaporized and mixed with the carrier gas. There followed a continuous transfer of the test sample into the thermal reactor during the period of the temperature rise programmed for the insertion chamber. The effluent products from the thermal reactor were collected in the cold trap located just inside the wall of the GC. With the switching of carrier gas to helium, the GC analysis step followed; the analysis was initiated by pressing the injection switch on the CDS-111 computer at the same time that the start button of the GC temperature programmer was depressed. A complete chromatogram of the product components as well as a tabulation of the peaks (retention times and peak areas) were obtained with the conclusion of the GC analytical run.

Each test run as described above yields a single point on the thermal decomposition plot (quantity of compound in the effluent vs. temperature of the thermal reactor, with the residence time kept constant) for the POHC material. Corresponding single points for each PIC material formed in significant quantity during the thermal treatment run are simultaneously obtained. Runs made over a series of temperatures can produce a thermal decomposition profile of the POHC and formation-decomposition profiles for various PICs, within the temperature limits investigated.

Because of the integrated arrangement of the thermal reactor and the gas chromatograph, calibrations with known standards at a non-decomposing temperature in the reactor, such as 300°C, are needed in attempting to identify the PICs produced during a regular run on a POHC substance. The peak retention times of the GC chromatogram help identify the particular compounds; the peak areas, as recorded on the CDS-111 computer tape, resolve the quantities of the various compounds by comparison to the values measured for the standards.

RESULTS

The series of runs made on various organic compounds are discussed for each compound investigated. Much of the investigative effort focused on chloroform because of the many PICs generated from its thermal treatment and the high concentrations of some of the PICs.

The common set of conditions used for the GC analysis step in most of the runs included:

(1) J&W fused silica capillary column, 15m x 0.262 mm with a liquid phase (film) of SE-30, 0.25 μm thick
(2) Carrier gas of helium at approximately 30 cm/sec and 1.5 atmosphere inlet pressure in the column, from a 1:30 splitter
(3) FID detection
(4) Temperature program of:
    (a) Initial temperature of -50°C for one minute.
    (b) Rise of 15° C/min, for 13.33 minutes.
    (c) Final temperature of 250°C, held for 1 to 11 minutes

A. Pentachloronitrobenzene (PCNB), $C_6Cl_5NO_2$

This compound was the first to be studied, for the purpose of determining the level of reproducibility obtainable with this TDU-GC system in comparison of the results to those reported by UDRI for the same compound.

The treatment of that POHC material was as follows.

The PCNB originally was prepared in a near-saturated solution in cyclohexane, and then 2-4 µl of that liquid was deposited by a syringe onto the end of the "solids" probe. After about ten seconds time for evaporation of the cyclohexane, the probe with its film deposit of PCNB was secured to the insertion chamber which then was heated to 300°C at a rate of 25°C/min. The resulting vapor was carried by a stream of air through the reactor at a flow rate calculated to provide a mean residence time of 2.00 seconds in the high-temperature zone. The cold trap, set in this case at -25°C as the initial temperature, was then heated in the ensuing GC temperature program to yield a chromatogram of individual component peaks as well as a tape record of peak times and area counts and area count percentages of the cumulative counts.

The thermal treatment temperatures ranged from 471°C to 571°C, which temperatures covered a span that had been shown in a previous report (2) to encompass the temperature decomposition profile (decomposition, to the >99.0% level, vs. reactor temperature) for that compound. Since the parent compound, pentachloronitrobenzene, was already totally decomposed (>99.99% Destruction Efficiency, DE) at the temperature of 571°C, no higher temperatures were investigated even though PIC compounds were present in substantial amounts.

The results of the GC analysis are presented in Figure 2 as a plot of reactor effluent "concentrations" vs. exposure temperature. Such concentration is accurately (directly) indicated in curve A which shows the increase in decomposition of the POHC material, the feed pentachloronitrobenzene, with increasing temperature. Curves B, C and D present the concentrations for the several, more abundant PICs that were produced during the thermal treatment process. Since component B was later identified as hexachlorobenzene (HCB), a known amount of reagent HCB was introduced as a feed to the TDU-GC system in a separate, low-temperature run to resolve the FID response of the gas chromatograph to that compound. That response was then used to accurately convert the peak area values (counts recorded on the CDS-111 computer tape) for HCB to equivalent concentration values. Since components C and D remained unknown, their peak area values have been presented as though they were directly related to PCNB concentrations, i.e., each area count for those peaks was given the same weight as each area count for the PCNB in calculating concentration values.

B. Chloroform, $CHCl_3$, in oxygen-rich atmosphere

In order to evaluate the TDU-GC system for handling a lower molecular weight, more volatile organic compound, chloroform was treated as a POHC material.

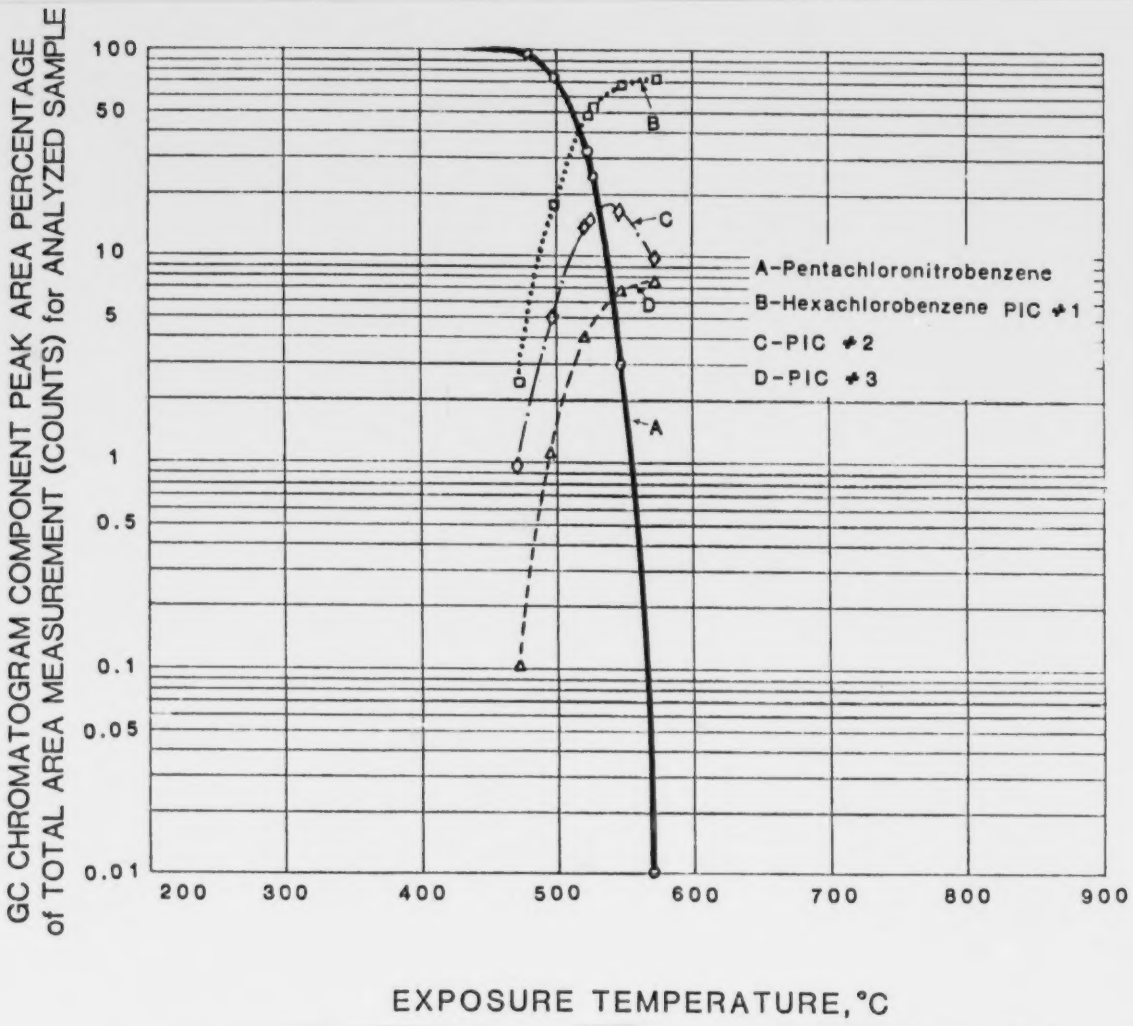

Figure 2. Thermal Treatment of Pentachloronitrobenzene, PCNB

In the early series of runs with chloroform, the compound was introduced first in vapor form at a concentration of 1 μg chloroform per 10 μl air in the sample. When a 10 μl sample of that chloroform-spiked air was directly injected into the carrier gas stream of the insertion chamber, the subsequent GC analysis of the effluent from the reactor set at a low temperature produced an inadequately small response on the chromatogram for that quantity of chloroform present in the sample. Subsequent samples of 50 μl (5 μg chloroform) and 100 μl (10 μg chloroform) of the vapor resulted in far more substantial peaks which, nevertheless, were considered to be too small for a decomposition study; the FID detector was somewhat insensitive to chloroform. The precision/accuracy of the results would be compromised for detecting those very small amounts of POHC remaining in the emissions after undergoing substantial decomposition at the higher reactor temperatures, as well as for detecting the lesser amounts of PICs formed.

In a later series of runs, much larger amounts of chloroform were introduced into the insertion chamber in quantities of 0.10 μl (~150 μg chloroform) and 0.20 μl (~300 μg chloroform) of the pure liquid phase. Like the vapor samples in the earlier series, the liquid samples were injected through a septum directly into the carrier gas (air) stream in a confined region where a plug of quartz wool helped to wipe off the tip of the syringe after the injection step and to disperse the injected liquid for effective vaporization. The insertion chamber was programmed to heat up to 125°C at a rate of 10°C/min. Residence time in the high-temperature zone of the reactor was controlled at 2.00 seconds through adjustment of the carrier gas flow. The cold trap for the effluent gas was cooled to -50°C as the starting point for the GC analysis program. The usual GC chromatogram and tape record (CDS-111) of peak times and area counts and percentages were obtained from each run.

The results from the series of runs using liquid chloroform feed are presented in the decomposition profile seen in Figure 3. Since the PICs shown in the figure were identified, each of the compounds (PICs) was used in calibration runs to obtain the ratio between peak area on the chromatogram and the amount of compound introduced to the TDU-GC system. Thus, the amount of a compound present in the emissions could be presented as a mol percent value referred back to the original amount of POHC material fed to the TDU-GC, as shown in Figure 3. The increased decomposition of the chloroform with increasing temperature in the thermal reactor produced major quantities of several PICs. Each of the PICs shown in Figure 3: hexachloroethane (C_2Cl_6), tetrachloroethylene (C_2Cl_4), and carbon tetrachloride (CCl_4), was identified by retention time checks with the corresponding component introduced individually as the feed in subsequent calibration runs. Minor quantities of other PIC compounds were observed. The highest reactor temperature investigated was 625°C, at which level essentially total destruction (>99.99% DE) of the POHC (chloroform) had occurred.

C. Chloroform, $CHCl_3$, in heptane, C_7H_{16}

In order to relate more directly to actual conditions of the incineration of chlorinated compounds, chloroform as one of several organic com-

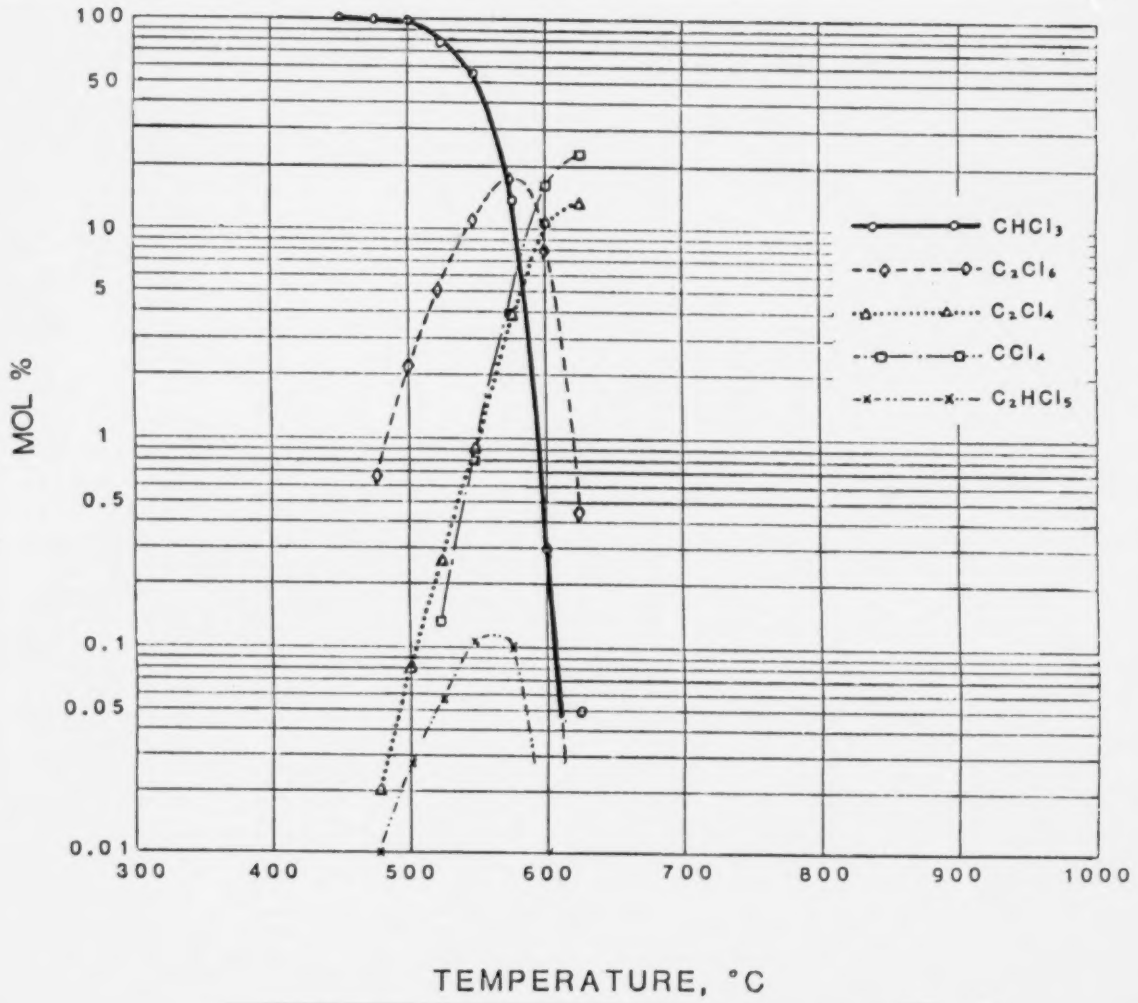

Figure 3. Thermal Treatment of Chloroform, $CHCl_3$
(Liquid feed, Air carrier gas)

pounds that might be found in a feed mixture, was selected for mixture (solution) in "fuel" heptane to undergo thermal decomposition treatment.

As a first step, heptane alone was investigated at various temperatures to characterize its decomposition, Figure 4. For the plot of the single compound (POHC) fed to the thermal reactor, as shown in Figure 4, the percent (value) of the POHC remaining in the emissions at the various reactor temperatures can be equally expressed as mol percent or weight percent. The higher temperature of 675°C was considered adequate to cover the temperature high for "total" chloroform decomposition, namely the 625°C observed in Figure 3. Then, three weight percent of chloroform was added to heptane to determine the effects of the presence of the heptane in the feed, upon the decomposition profile of the chloroform. The feed, whether pure heptane or chloroform-spiked heptane, was introduced into the insertion chamber as a liquid.

The chromatogram for a sample of heptane that was exposed to a low, non-decomposing temperature level showed a very considerable number of contaminant peaks throughout the temperature program range of the GC analysis. Many of those peaks persisted even at higher temperatures where heptane began to decompose.

Subsequent runs of the three weight percent of chloroform in heptane yielded chromatograms in which chloroform and its decomposition products were completely (concentration level wise) masked by the heptane-source components.

D. Chloroform, $CHCl_3$, in reduced-oxygen atmosphere

A series of tests was used to investigate chloroform at an oxygen concentration greatly reduced from that of the usual conditions that prevailed in the earlier runs, cited in "B" above; the reduced oxygen concentration is represented by a ϕ of 0.76 (ratio of the stoichiometric oxygen requirement to the actual oxygen available for reaction with the organic compound). At the same time, the range of temperatures investigated was extended to 850°C (as compared to the high of 625°C in B above).

To execute the condition of reduced oxygen atmosphere, a 1-liter flask was used to prepare the desired ratio of oxygen to POHC (chloroform). Initially, the flask was left open overnight to room air. Then it was sealed with a glass stopper, and a calculated amount of liquid chloroform was injected into the flask through a septum in the stopper to produce a mixture of chloroform vapor and air that represented an equivalence ratio, ϕ, of 0.76. The flask was allowed to stand for an hour or more to get uniform distribution of the chloroform vapor before a gas sample was drawn. A second port with a clean septum was used for the gas sampling to prevent contamination of the syringe needle by a film residue of liquid chloroform that might have been left in the septum used earlier for injection of the liquid chloroform into the flask. Before that first vapor sample was drawn, however, a syringe needle was inserted through the first septum to depressurize the flask to room atmosphere from the pressure built up by vaporization of the liquid chloroform. Successive vapor samples were drawn

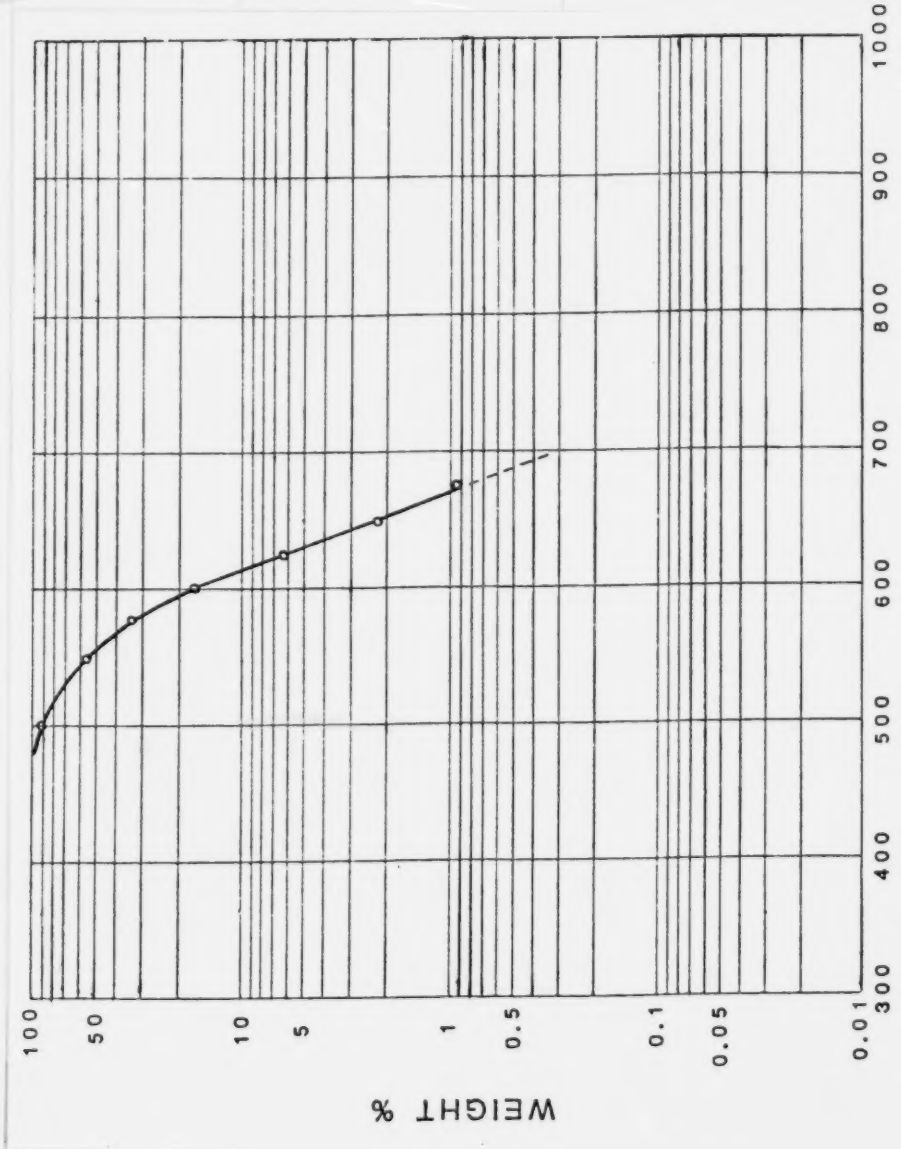

Figure 4. Thermal Decomposition of Heptane

through the second septum for the various test runs.

To perform all the runs needed to develop the picture (plot) of chloroform decomposition along with PIC formation and decomposition, the extensive range of temperatures required 2-3 days of test runs. Instead of preparing a new batch of chloroform vapor for each day's quota of runs, as had been done for earlier study series, the same vapor supply preparation was used throughout for all the runs in the chloroform series with air as the carrier gas. During that particular series, it was discovered that the chloroform vapor concentration in the supply flask decreased with time; each day of those involving high-temperature runs, a sample of the prepared vapor was run through the TDU-GC system at a low, non-decomposing temperature in the reactor to obtain a reference concentration for that day. That concentration was compared to the original that was obtained on the first day in order to get corrected values of the emissions components measured in test runs on the ensuing days.

The vapor preparation in the flask was saved for a period of nearly two weeks expressly for periodic samplings to obtain concentration values that would show the degradation of the chloroform with such extended time. A plot, relative concentration in the flask vs. time, is shown in Figure 5.

The flask had been covered with aluminum foil during that period to reduce the degradation that might have resulted from exposure to light.

Samples, 100 μl, of the flask vapor were introduced by syringe into the insertion chamber of the TDU-GC, with an inert (non-oxygen containing) gas stream used to transfer the vapor sample through the thermal reactor. The syringe plunger was depressed slowly, over a period of no more than 30 seconds, in order to prevent condensation of the vapor in the barrel of the syringe that might have occurred with the pressure increase of instantaneous injection.

Two series with inert gas were run, one with helium as the carrier and the other with nitrogen. In each case, a filter in the supply line of carrier gas was used to remove any oxygen or water vapor that might be present in the supply of the inert gas. In each series, a chloroform-oxygen mix of $\phi = 0.76$ was used.

In a third series, the same vapor preparation was duplicated for comparison to the two previous "inert gas" series. However, in this latest series, air was used as the carrier gas so that the oxygen available for interaction with the sample organic compound (chloroform) was far in excess of the stoichiometric amount needed for complete "combustion" of that compound. Otherwise, all test conditions for the three series were the same.

The decomposition plots for the three series are shown in Figure 6 (helium as the carrier gas), Figure 7 (nitrogen as the carrier gas), and Figure 8 (air as the carrier gas).

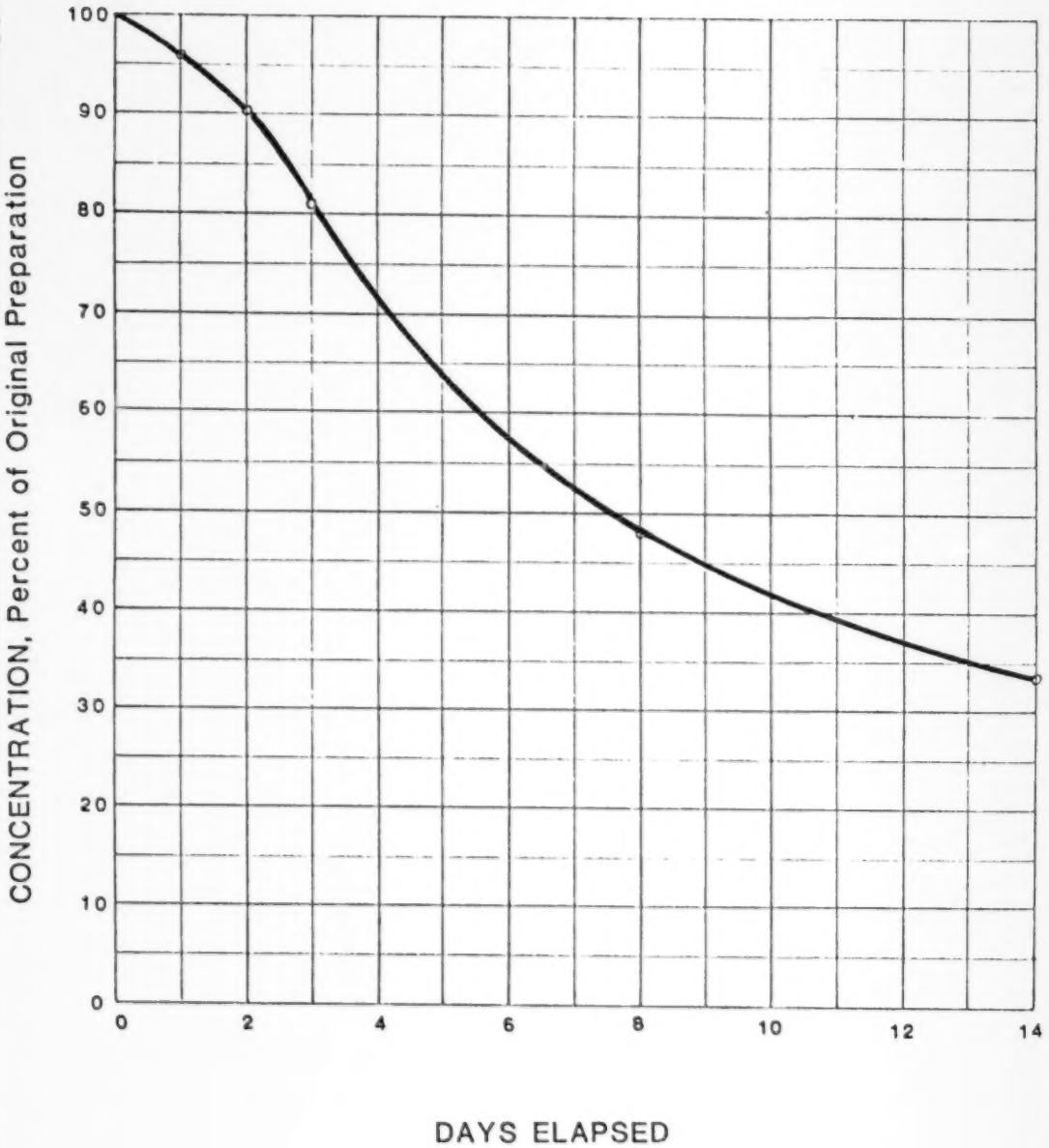

Figure 5. Degradation of Chloroform Vapor Supply

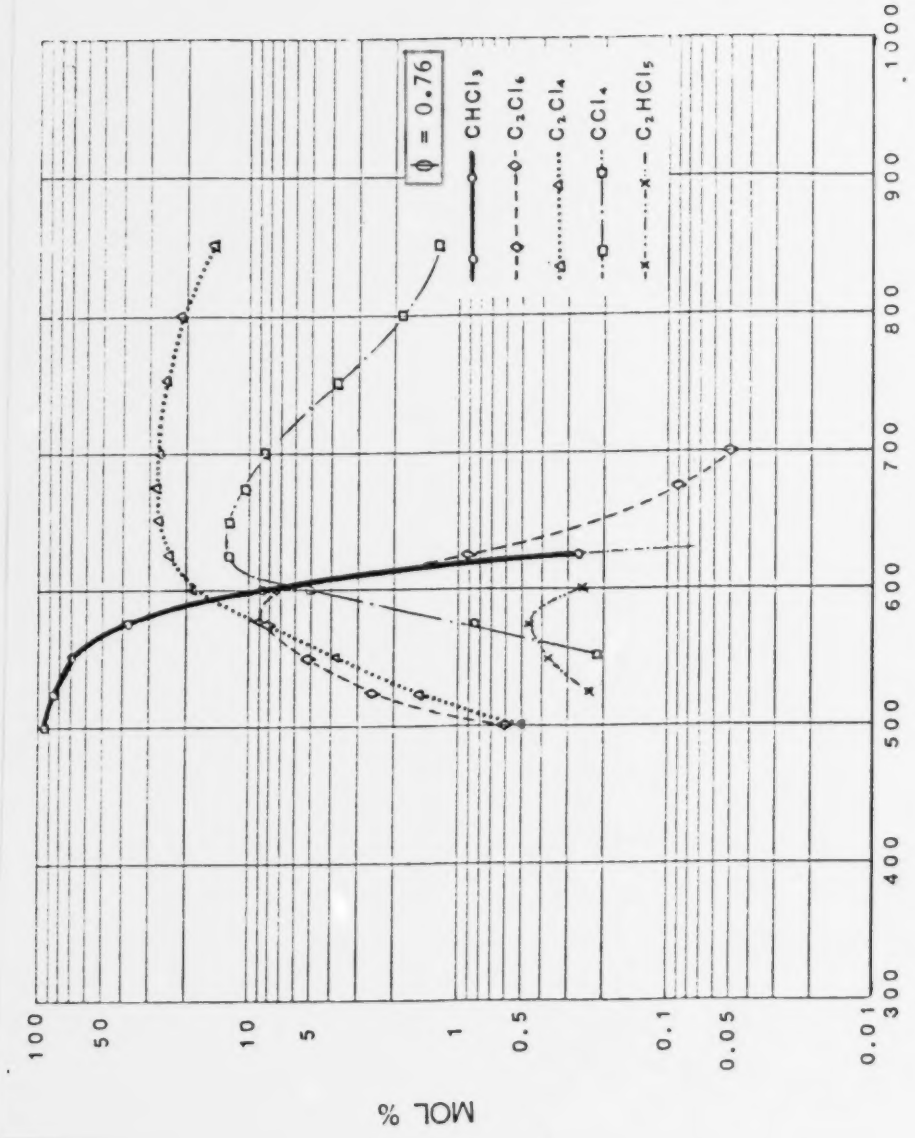

Figure 6. Thermal Treatment of Chloroform, $CHCl_3$ (Vapor feed, Helium carrier gas)

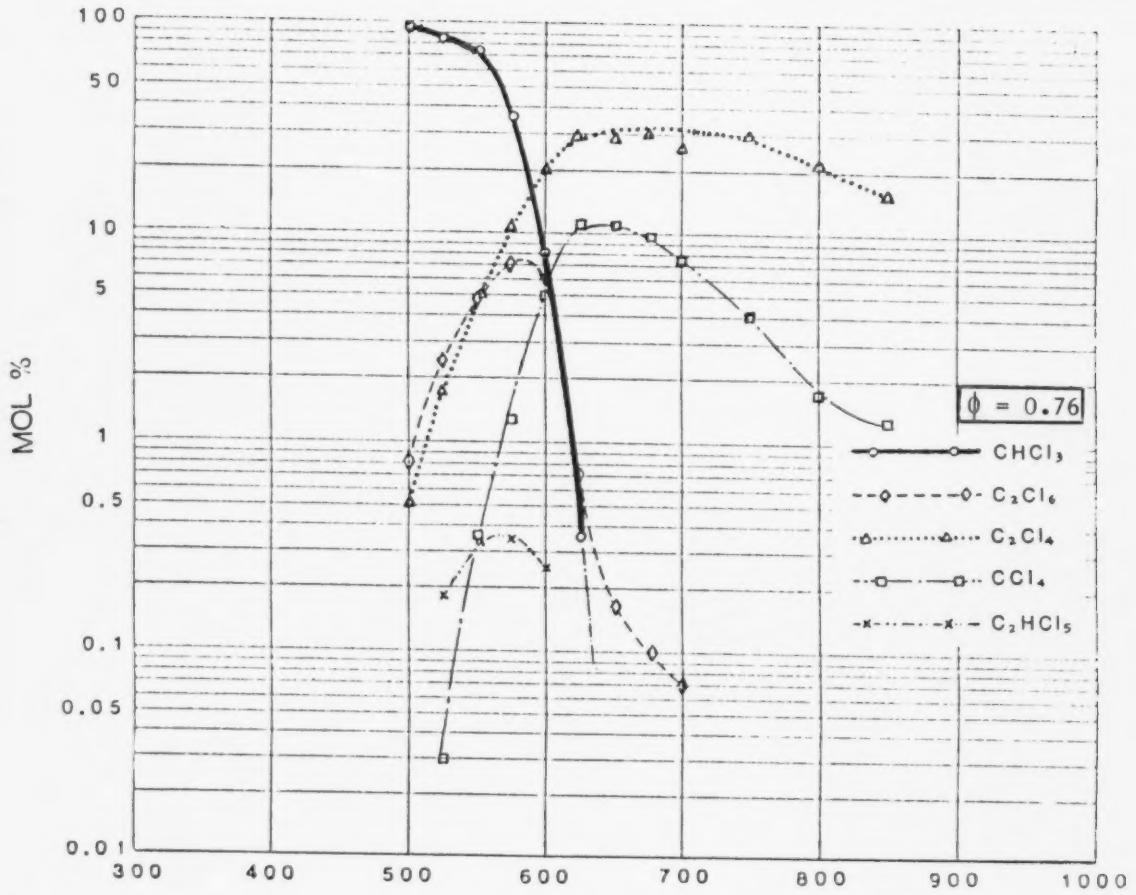

Figure 7. Thermal Treatment of Chloroform, $CHCl_3$
(Vapor feed, Nitrogen carrier gas)

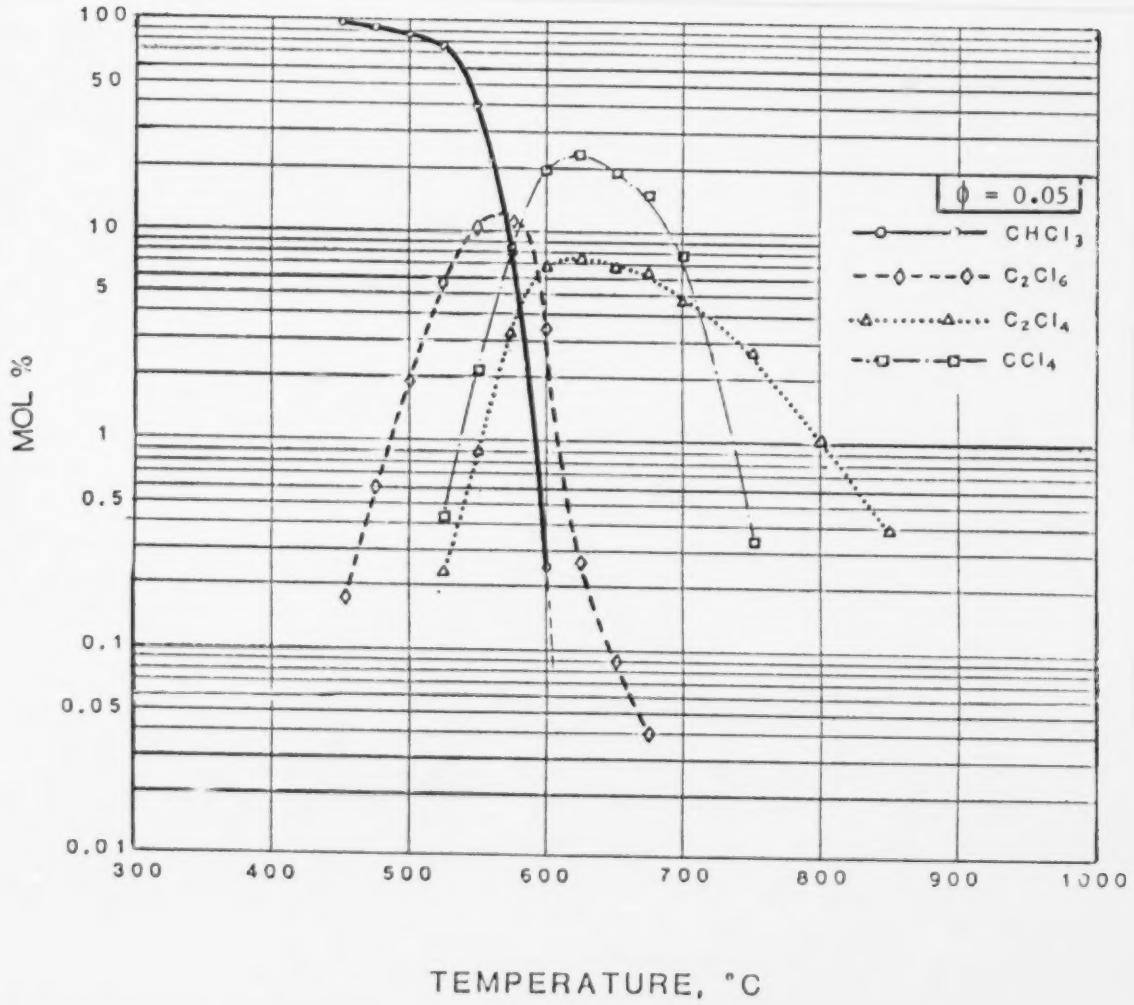

Figure 8. Thermal Treatment of Chloroform $CHCl_3$
(Vapor feed, Air carrier gas)

E. Carbon tetrachloride, CCl_4, in reduced-oxygen atmosphere

Carbon tetrachloride as a POHC at a ϕ of 0.60 was individually exposed to thermal treatment in the TDU-GC to provide information that would supplement the findings for carbon tetrachloride as a PIC generated in the thermal treatment of chloroform in the previously cited series.

The same vapor flask preparation procedure was used to produce carbon tetrachloride vapor for this study. Helium was the carrier gas during the TDU-GC runs.

The thermal treatment plot for carbon tetrachloride as a single component feed (POHC) is shown in Figure 9. In Figure 10, the plot for carbon tetrachloride as a POHC is superimposed on the plot showing carbon tetrachloride as a PIC produced during the thermal treatment of chloroform under the same condition of helium being used as the carrier gas.

F. Freon-113, CCl_2 F- $CClF_2$, in oxygen-rich atmosphere

The study of Freon-113 called for quick injection of the liuqid phase directly into the insertion chamber by means of a syringe, with air as the carrier gas. The ϕ for the oxygen-rich runs was 0.05.

The thermal decomposition profile for this compound is shown in Figure 11. The PICs detected were minimal, with only one peak of significant height showing up in the chromatogram.

G. Monochlorobenzene, C_6H_5Cl, in oxygen-rich atmosphere

Because of the moderately high boiling point of monochlorobenzene, the mini-injector syringe used to meter out the tiny quantity (0.05 µl) of the liquid was left in the insertion chamber until the end (300°C) of the temperature program. As usual, the carrier gas was air.

The thermal decomposition profile for the compound is shown in Figure 12. There were no PICs of any signicant quantity measured/detected in the emissions.

H. Trichloroethylene, C_2HCl_3, in oxygen-rich atmosphere

The introduction of trichloroethylene feed into the TDU-GC system was similar to that for monochlorobenzene, cited above, i.e., 0.05 µl of the liquid from a mini-injector syringe that was retained in the insertion chamber until the 300°C level of the temperature program was reached.

The thermal decomposition profile for this compound is shown in Figure 13.

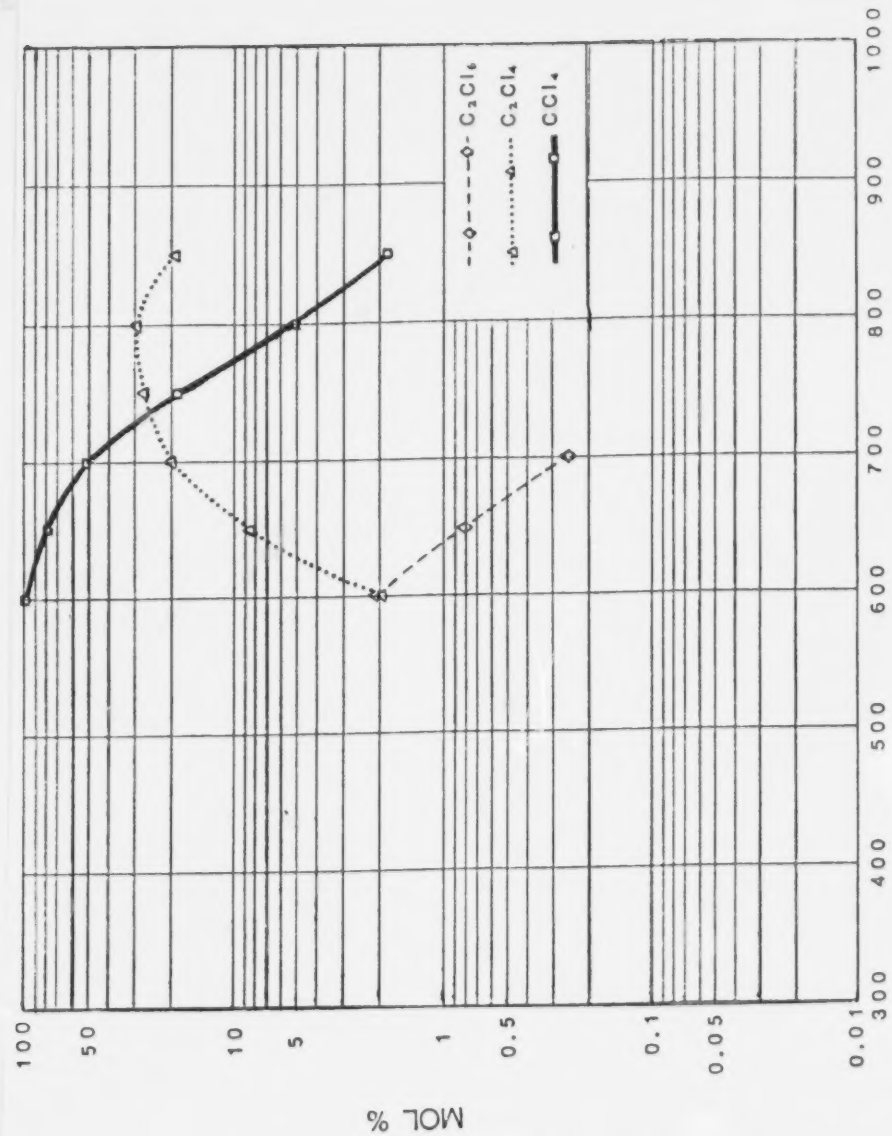

Figure 9. Thermal Treatment of Carbon Tetrachloride (Vapor feed, Helium carrier gas)

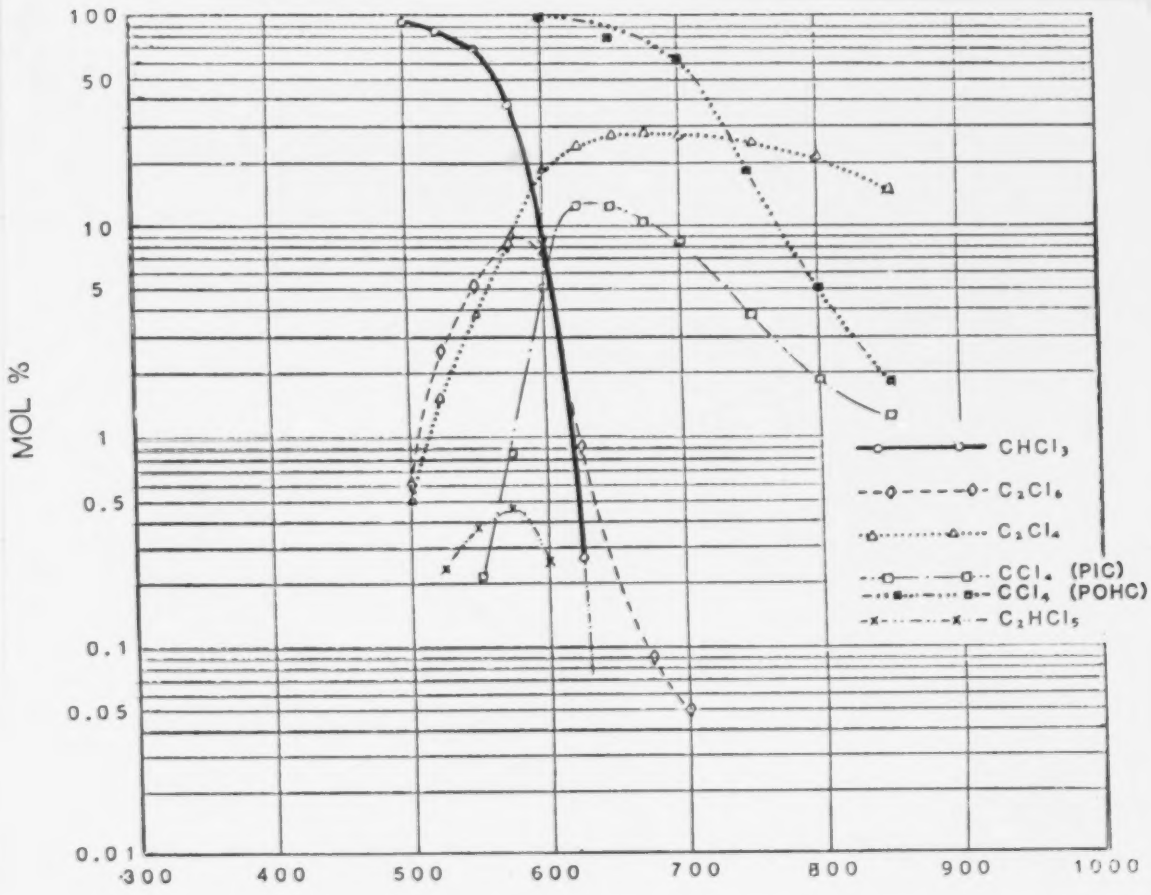

Figure 10. Thermal Treatment of Chloroform, $CHCl_3$ (Vapor feed, Helium carrier gas) + Carbon Tetrachloride as a POHC

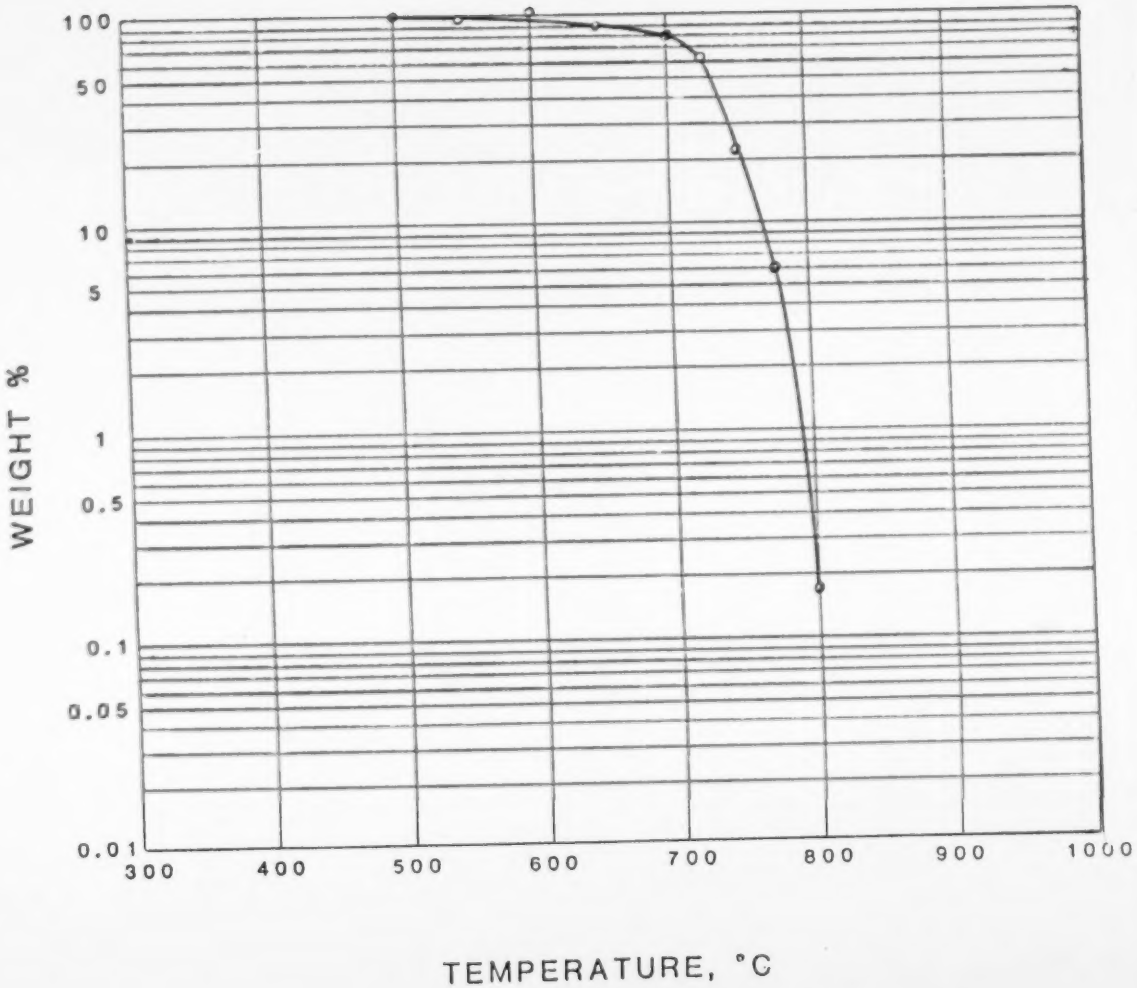

Figure 11. Thermal Decomposition of Freon-113

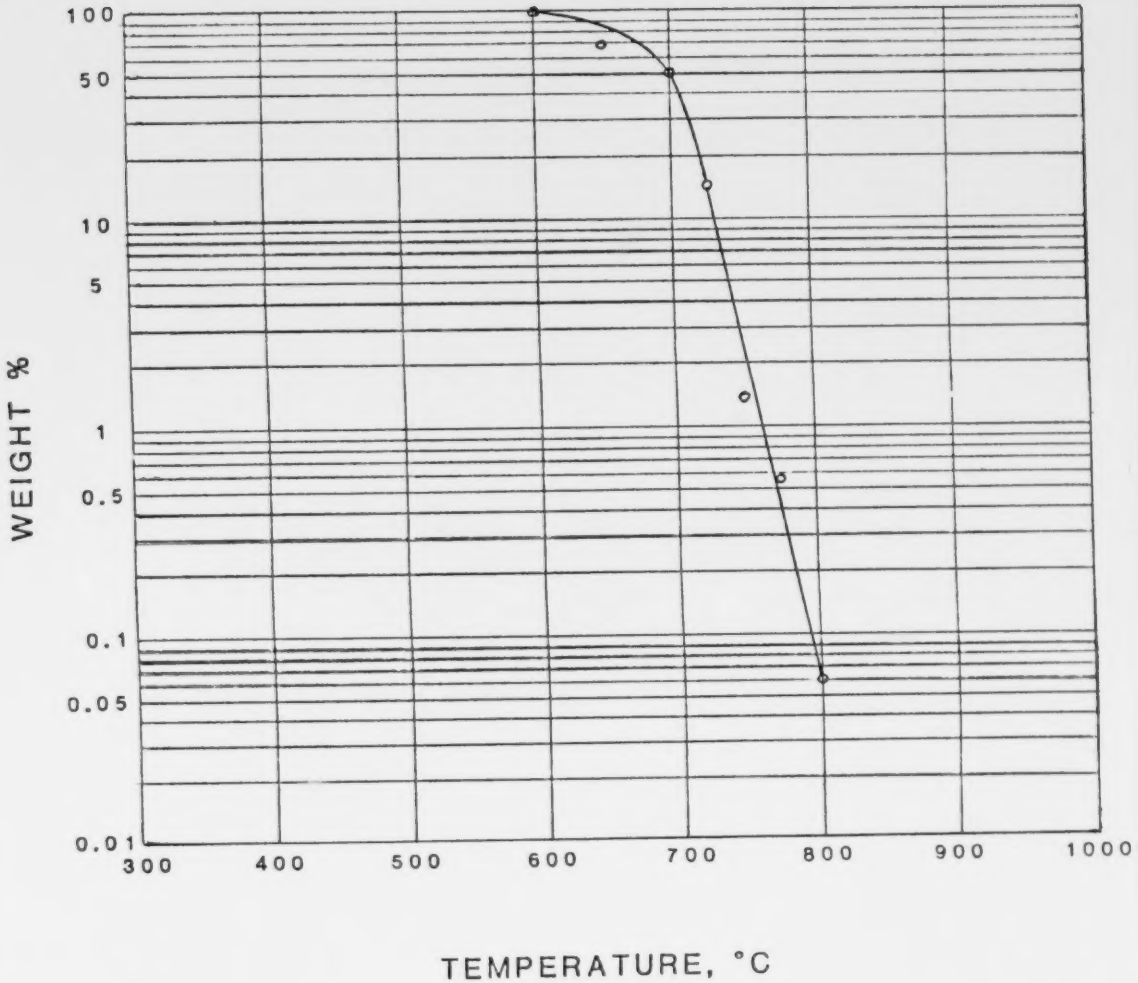

Figure 12. Thermal Decomposition of Monochlorobenzene

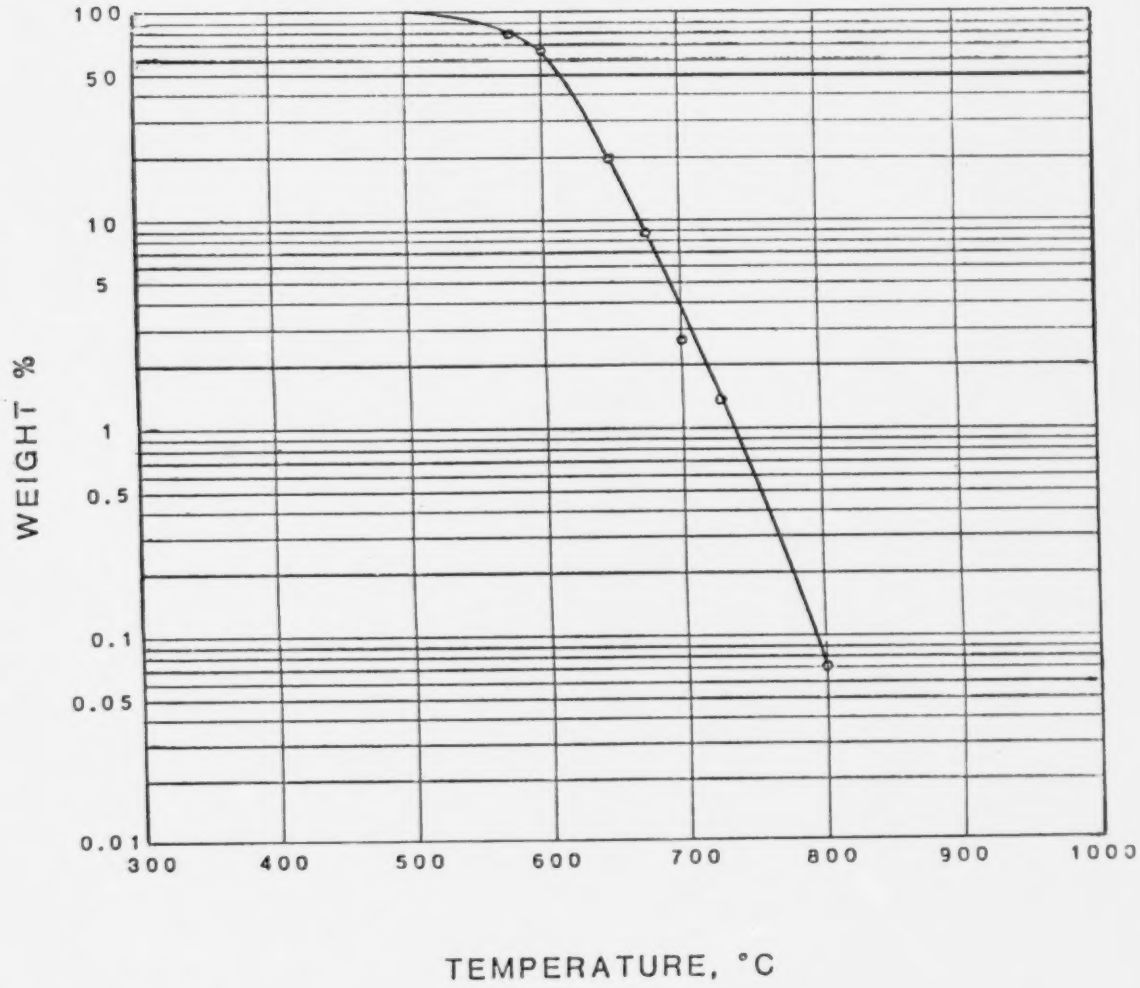

Figure 13. Thermal Decomposition of Trichloroethylene

DISCUSSION

A. Pentachloronitrobenzene, PCNB

This compound was selected in the initial work with the TDU-GC primarily to check the reproducibility of results in comparison to those obtained in the earlier work (2,3) performed at UDRI. In their work on pentachloronitrobenzene, UDRI presented the results for PCNB and its principal PIC compound, identified as hexachlorobenzene (HCB), as shown in Figure 14.

The results from the current study showed a decomposition curve for PCNB that closely matched the curve reported by UDRI for similar test conditions; the close match is evident by comparing Figure 14 with Figure 2. The extrapolated value for PCNB at 99.99% DE (i.e., the 0.01 percentage level in the plot, Figure 14) in the UDRI results occurred at about 570°C which value coincides with that for the current study, Figure 2. PIC compounds B, C, and D, which appeared in abundant quantities, are also shown in Figure 2, with B identified as hexachlorobenzene. The hexachlorobenzene formation/decomposition profile, curve B, also closely matched that reported by UDRI.

B. Chloroform in oxygen-rich atmosphere

The study of reproducibility of results was extended to the use of chloroform, a volatile liquid organic compound in contrast to the non-volatile solid pentachloronitrobenzene.

UDRI presented results from their early work with chloroform in the plot of Figure 15 which shows three PICs that were not identified at that time. Since then UDRI had expanded their investigation of chloroform to such extent where a multiplicity of PICs were detected and, indeed, most of them identified.

The results of the current study (Figure 3) show a decomposition profile for the feed material, chloroform, that closely fit the curve obtained by UDRI (DE 99.99 of 625°C compared to UDRI's 615°C). Also, the formation-decomposition curves for the principal PICs are generally similar to those of the "unknowns" in the UDRI plot, both in shape (rate of change in concentration with temperature) and in relation to the temperature levels. The three PICs shown in the plot for the current work have been identified, as noted in Figure 3, namely hexachloroethane (C_2Cl_6), tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4); the identification was made according to retention times for the respective peaks of the GC chromatogram.

It is evident from the chlorine-saturated state of each of the PIC molecules (C_2Cl_6, C_2Cl_4, and CCl_4) identified in major concentrations, that the hydrogen atom present in the parent chloroform molecule was being thoroughly eliminated from the organic product species.

It has been suggested that the initial step in chloroform decomposition involves the direct loss of HCl with the formation of the inter-

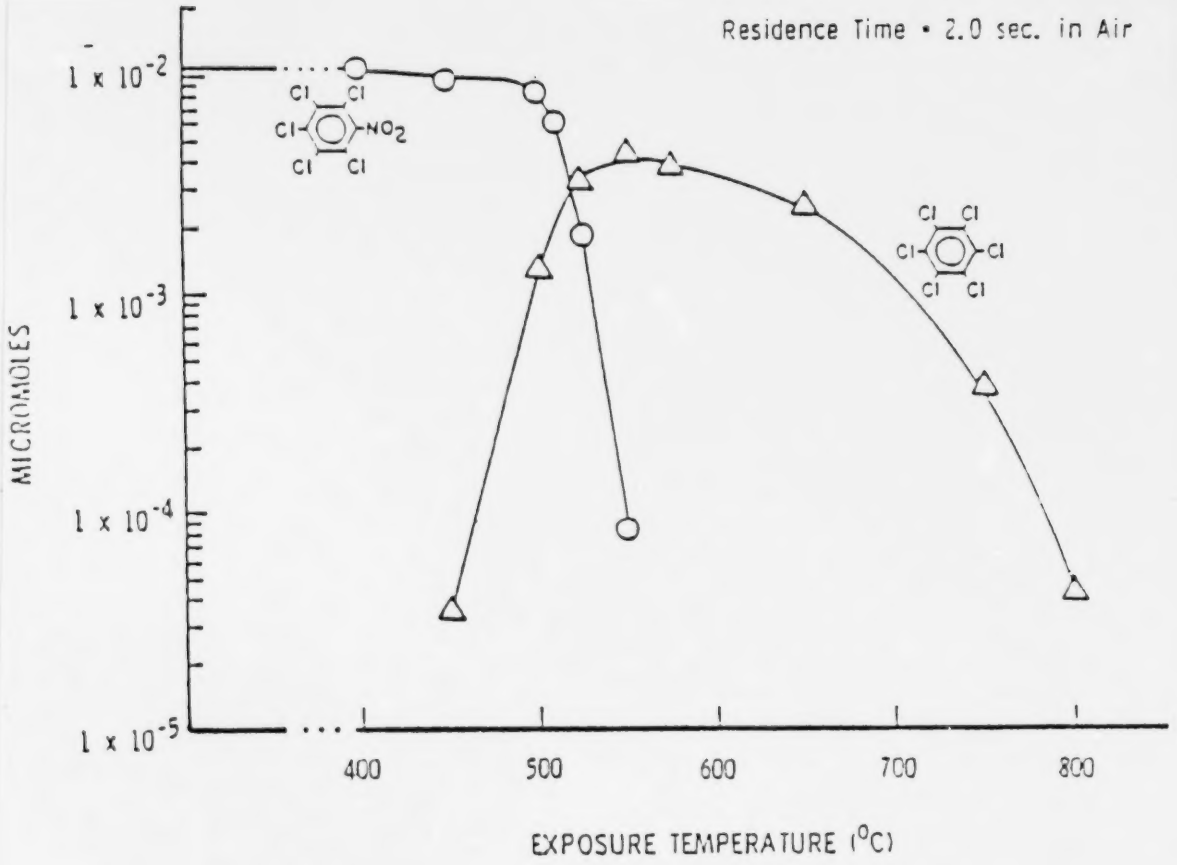

Figure 14. Thermal Decomposition Profile of Pentachloronitrobenzene Per UDRI (7).

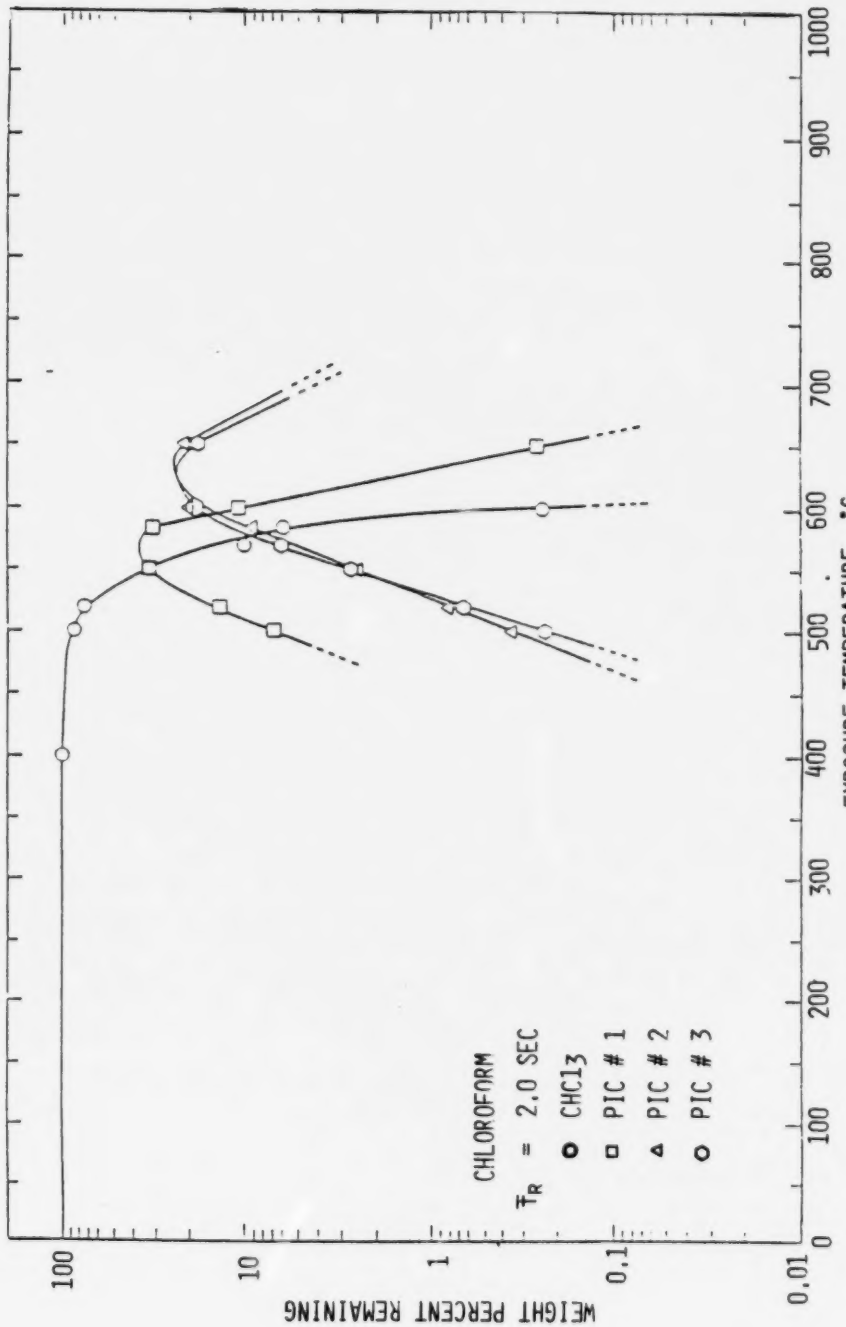

Figure 15. Thermal Decomposition Profile of Chloroform Per UDRI (7)

mediate biradical dichlorocarbene (7):

$$CHCl_3 \xrightarrow{\Delta} : CCl_2 + HCl \qquad (1)$$

followed by the reaction of that radical with chloroform to form pentachloroethane:

$$: CCl_2 + CHCl_3 \longrightarrow C_2HCl_5 \qquad (2)$$

UDRI reported that chloroform and pentachloroethane are of comparable stability, i.e., that both those compounds had similar decomposition profiles within the same temperature range (7).

Under the conditions of the current series of runs, the presence of pentachloroethane was not detected/observed at all, not even in the initial stages of chloroform decomposition. If pentachloroethane was formed, it must have immediately (within the 2.0 seconds residence time in the high temperature zone) reacted to form other compounds, such as tetrachloroethylene, that indeed were detected/measured in significant quantities. It is likely that a mechanism different from that indicated above (formation of the dichlorocarbene) prevailed in the selective removal of the hydrogen atom of the chloroform molecule from further interaction and incorporation in the chlorinated compounds detected in the emissions. Probably that result was due to the high oxygen/organic compound ratio established in the current study conditions, with molecular oxygen acting as the source reactant for eliminating the hydrogen. The decomposition of chloroform to form the $CCl_3^{\bullet}$ radical would be promoted by simple radical mechanisms, as in:

$$CHCl_3 + OH^{\bullet} \longrightarrow CCl_3^{\bullet} + H_2O \qquad (3)$$

followed by:

$$CCl_3^{\bullet} + CCl_3^{\bullet} \longrightarrow C_2Cl_6 \qquad (4)$$

which hexachloroethane product was observed to form quite readily, with measurable amounts being formed at less than 450°C, well before any other organic product was detected (see Figure 3). On the other hand, with the further increase in temperature (to 625°C), the hexachloroethane just as readily decomposed. Elimination of molecular chlorine, Cl_2, from the hexachloroethane molecule would enhance the production of tetrachloroethylene:

$$Cl_3\,C\,C\,Cl_3 \xrightarrow{\Delta} Cl_2\,C = C\,Cl_2 + Cl_2 \qquad (5)$$

Ready decomposition of the Cl_2 molecule would boost the concentration of $Cl^{\bullet}$ atoms that could then react with the $CCl_3^{\bullet}$ radicals produced from the initial decomposition of chloroform, to form carbon tetrachloride:

$$Cl_2 \rightleftharpoons 2Cl^{\bullet} \qquad (6)$$

$$Cl^{\bullet} + C\,Cl_3^{\bullet} \longrightarrow C\,Cl_4 \qquad (7)$$

Only perchlorinated compounds - hexachloroethane (C_2Cl_6), tetrachloro-

ethylene (C_2Cl_4), and carbon tetrachloride (CCl_4) - were produced in signifcant amounts, to a degree that accounted for more than fifty weight percent of the original chloroform charge when peak levels of the PICs were established. There were only trace amounts (less than 0.1 percent) of unidentified PICs, which PICs may have contained hydrogen. Thus, while the plot shows a very appreciable accounting of the carbon and chlorine of the feed chloroform, in the product PICs at the various temperatures investigated, there was no such extensive accounting for the hydrogen.

The same values that were used to develop the plotted curves for the four compounds seen in Figure 3 were translated into the plots presented on a different, a linear, scale in Figure 16. Thus, Figure 16 presents the results of the thermal treatment of chloroform on a rectangular (linear) scale instead of the semi-log scale of Figure 3. The 4-cycle log scale of Figure 3 spans the four decades of concentration of compound that focus on the 99.99% Destruction and Removal Efficiency (DRE) limit factor. Figure 16, on the other hand, clearly shows the comparative amounts of compounds present in the emissions from the thermal reactor.

The curves of Figure 16 readily indicate the relatively large amounts of potentially toxic PICs being evolved from the decomposition of the parent compound, chloroform. From such a typical, standard, graphical display, the health effects investigator, among others, can more readily grasp the impact of the thermal reaction process upon pollutants released to the environment.

It is evident from Figure 16 that the concentration of hexachloroethane (C_2Cl_6) has peaked at a temperature ($\sim$570°C) where the tetrachloroethylene (C_2Cl_4) and carbon tetrachloride (CCl_4) are just beginning to form. The simultaneous production (and rate) of the latter two compounds suggests that a common mechanism producing those two compounds at the same time may be in effect at those temperature levels and test conditions.

C. Chloroform in heptane

At the operating concentrations of three weight percent chloroform in heptane, the GC peaks for chloroform and its thermal decomposition products were effectively masked by the pollutants from the heptane feed. Perhaps a tenfold increase in chloroform would manifest the presence of that compound in the emissions stream passing to the GC detector. Even then, such compounds as tetrachloroethylene and carbon tetrachloride would not be resolved satisfactorily, if at all, in the emissions. Consequently, the study of the thermal treatment of chloroform in heptane was suspended because of the extraordinary adjustments in feed mixture composition that would be necessary to obtain meaningful analyses during the various test runs.

A decomposition profile was, however, obtained for the heptane, Figure 4. It is evident that decomposition began at a temperature slightly greater than 450°C. The rate of decomposition shows itself as a substantially straight line plot of moderate slope on the semilog scale so that by 675°C

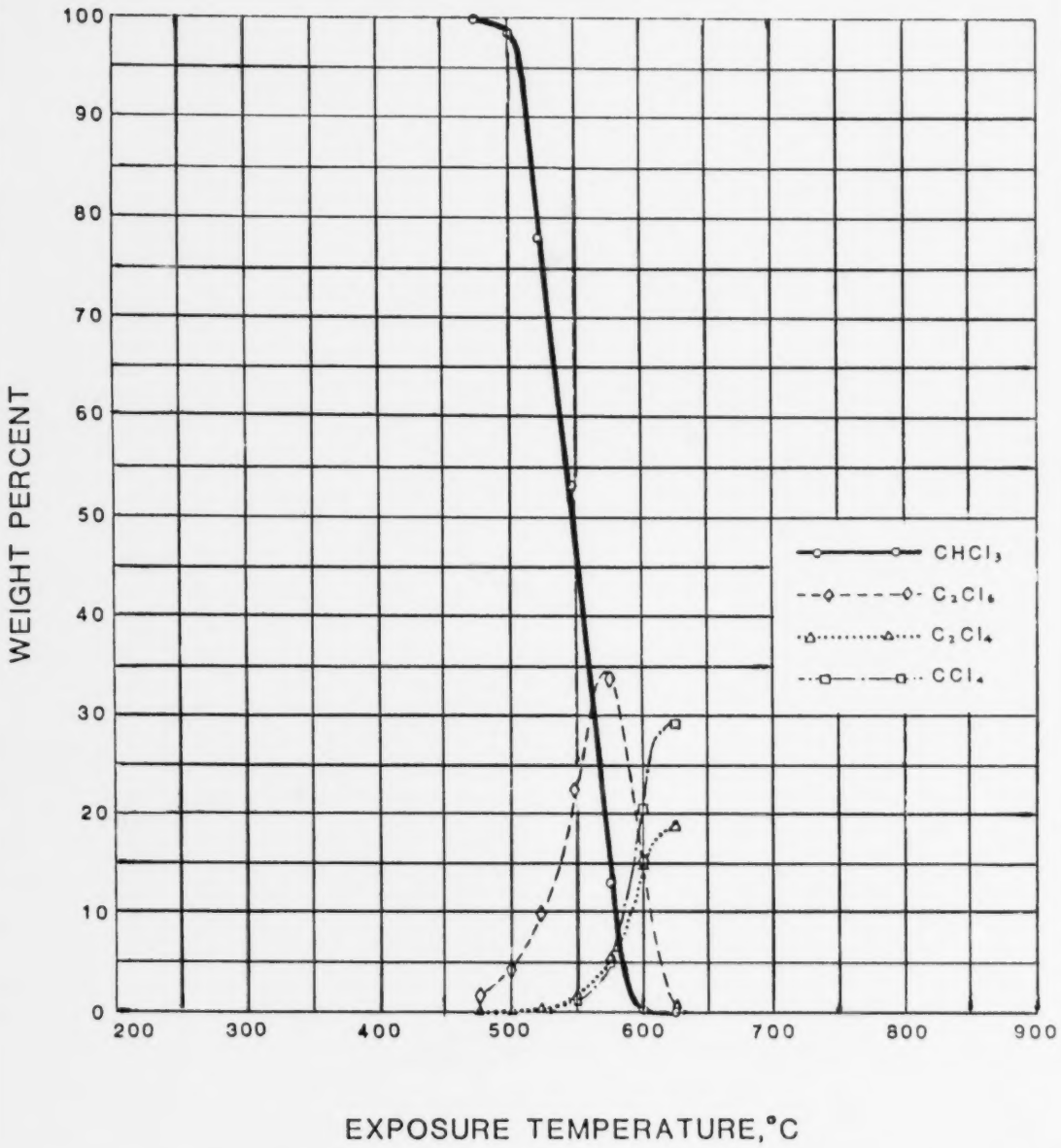

Figure 16. Thermal Treatment of Chloroform
(Rectangular Scale)

a little more than one percent of the heptane still persists in the effluent stream from the reactor. The 675°C level represents a temperature excess of 50° over the 625°C projected for 99.99% DE of chloroform as determined in the previous study.

D. Chloroform in "reduced" oxygen atmosphere

The series of runs with chloroform at the reduced oxygen concentration of $\phi = 0.76$ revealed several significant changes in results as observed previously for chloroform in a highly oxidative atmosphere in the thermal reactor zone.

In the first series of reduced oxygen runs, helium was used as the carrier gas. When there were observed the large differences from results in the oxidative atmosphere with chloroform fed as a liquid to the insertion chamber, a second series was run with nitrogen as the carrier gas.

To obtain a comparison with an oxidative atmosphere in the reactor over the more extensive range of temperatures (i.e., up to 850°C) investigated under the reduced oxygen condition, a series duplicating the vapor feed condition of the helium and nitrogen carrier gas series was carried out with air as the carrier gas.

A comparison of the results of the reduced oxygen atmosphere of $\phi = 0.76$ when helium and when nitrogen were used, with those of the highly oxidative atmosphere of $\phi = 0.05$ showed the following differences, some of which were remarkably large.

(1) Tetrachloroethylene, C_2Cl_4, was far more refractory under the reduced oxygen condition. Its presence persisted in large amount throughout the higher temperatures investigated. At the 850°C level, there still was about 15 mol percent of the compound present in the emissions (Figure 6), in sharp contrast to the 0.4 percent in the rich oxygen atmosphere case (Figure 8). Also, the C_2Cl_4 formation began earlier, at about the same time as C_2Cl_6, and peaked at about 30 mol percent generated at the 675-700°C level, as compared to only 7 percent at 625°C in the rich oxygen situation, with a much later "takeoff".

(2) Carbon tetrachloride, CCl_4, peaked at a lower concentration of 11-13 mol percent in the reduced oxygen runs (about 23% in the rich oxygen) but persisted through the higher-temperature exposure much more than in the oxygen-rich case where the concentration dropped off sharply in the 650 to 750°C range (Figure 8).

(3) The hexachloroethane, C_2Cl_6, showed a similar pattern in both the reduced oxygen and the rich oxygen atmsopheres, with an early build-up of concentration followed shortly by almost total elimination at the 700°C level.

(4) Pentachloroethane, C_2HCl_5, appeared in little more than trace amounts in both the helium and nitrogen runs, but was not detected in the

air carrier gas run with the vapor feed of chloroform.

(5) The POHC chloroform appeared to have a slightly higher (extrapolated) value of about 635°C for the 99.99% DE point in the reduced oxygen cases (Figures 6 and 7) as compared to about 610°C in the rich oxygen case.

It is concluded that oxygen in large amount had a very significant effect upon the composition of the emissions under the test conditions used. Only perchlorinated compounds were being formed in significant/detectable amounts in the reduced oxygen atmosphere, with both tetrachloroethylene and carbon tetrachloride persisting through the higher temperatures. The similar picture for hexachloroethane in reduced and in rich oxygen atmospheres indicates that it was far less sensitive to the presence of oxygen at the concentration levels studied, than were the other PICs; in either atmosphere, the hexachloroethane proved to be significantly less stable than the other perchlorinated PICs.

A simple degradation of chloroform involving the splitting off of a hydrogen atom:

$$CHCl_3 \xrightarrow{\Delta} CCl_3^{\cdot} + H^{\cdot} \qquad (8)$$

or of a chlorine atom:

$$CHCl_3 \xrightarrow{\Delta} CHCl_2^{\cdot} + Cl^{\cdot} \qquad (9)$$

followed by the attack of the $Cl^{\cdot}$ radical on another chloroform molecule:

$$CHCl_3 + Cl^{\cdot} \longrightarrow CCl_3^{\cdot} + HCl \qquad (10)$$

would supply the $CCl_3^{\cdot}$ radicals to readily form the hexachloroethane, as noted previously:

$$CCl_3^{\cdot} + CCl_3^{\cdot} \longrightarrow C_2Cl_6 \qquad (4)$$

The removal of HCl from the chloroform molecule, equation (1), on the other hand, would be the source of the dichlorocarbene bi-radical for producing tetrachlorethylene:

$$CHCl_3 \xrightarrow{\Delta} :CCl_2 + HCl \qquad (1)$$

$$:CCl_2 + :CCl_2 \longrightarrow C_2Cl_4 \qquad (11)$$

In the rich oxygen atmosphere, the hydrogen component of the organic compounds (e.g., the feed chloroform) is abstracted to such extent that reactions (8) plus (10) may be promoted at the expense of reactions (9) and (1) to enhance the production of hexachloroethane, reaction (4) and reduce that of tetrachloroethylene, reaction (11).

E. Carbon tetrachloride in "reduced" oxygen atmosphere

Carbon tetrachloride at a ϕ of 0.60 was tested for comparison of its

thermal decomposition profile as a POHC (i.e., feed) with the formation/decomposition plot of carbon tetrachloride produced as a PIC in the chloroform study, Figure 6. At the top temperature of 850°C, there still was nearly 2 percent of the carbon tetrachloride present in the emissions, even though decomposition had started at 600°C, Figure 9. Tetrachloroethylene was the major PIC produced, reaching a peak of nearly 35 weight percent (Figure 6). The emission level in the two series - carbon tetrachloride as a POHC and as a PIC from chloroform - approached a common value at the high temperatures.

The concentration values for tetrachloroethylene as a PIC resulting from the carbon tetrachloride decomposition were quite similar in the high temperature range to those observed in the chloroform decomposition series. It appears that tetrachloroethylene is a commonly produced PIC, whether from chloroform decomposition or from carbon tetrachloride decomposition or from the carbon tetrachloride produced as a PIC from chloroform decomposition, that displays a considerable stability at the high temperatures in a reduced oxygen atmosphere.

F. Freon-113, $C_2Cl_3F_3$, in oxygen-rich atmosphere

The thermal decomposition profile for Freon-113, Figure 11, is typical of that for most of the organic compounds investigated. Decomposition started at 500-550°C and proceeded at the usual slow rate of decomposition with increasing temperature and then sharply changed to a rapid rate as represented by the steeply sloping line for equal increments of increasing temperature. An extrapolated value of 810°C marks the 99.99% DE point.

G. Monochlorobenzene, C_6H_5Cl, in a highly oxidative atmosphere

Unlike Freon-113, monochlorobenzene showed a uniform rate of decomposition with increasing temperature on the semi-log plot, Figure 12. It appears to be more refractory than the Freon-113; the plot shows an extrapolated value of 850°C for the 99.99% DE point. The production of measured PICs was minimal, with less than 0.5 weight percent detected for any one PIC.

H. Trichloroethylene, C_2HCl_3, in highly oxidative atmosphere

From a study of test burns of tetrachloroethane in the Turbulent Flame Reactor (TFR), it was reported that trichloroethylene (TCE) was a persistent PIC in the emissions. It was often present in higher concentration than the POHC material, tetrachloroethane, and was considered to be a "quite stable compound" (8).

The evaluation of the stability of TCE with the TDU-GC yielded a thermal decomposition profile for a 2 seconds residence time that showed decomposition starting at about 550°C, Figure 13, with as much as 0.1 percent (only 99.90% DE) remaining in the emissions from the thermal reactor at 800°C. The 99.0 percent DE point occurred at 725°C, a full 175° higher than the starting point. This rate of temperature effect might be compared to that for hexachlorobenzene, for which UDRI reported onset of

thermal decomposition at 610°C and 99.9 percent DE at 810°C, a span of 200°C for that quite refractory compound. The $T_{99.99}$ (temperature for 99.99% decomposition) reported by UDRI occurred at 880°C. The extrapolated value for $T_{99.99}$ from the present TCE data indicated a like value, about 875°C, even though the onset of decomposition of TCE occurred about 50-60°C lower than that for hexachlorobenzene.

It appears, indeed, that TCE is a significantly thermally-stable compound.

SUMMARY and CONCLUSIONS

The Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) system has been used in thermal treatment of various organic compounds associated with the incineration of toxic/hazardous organic waste substances.

The system has been used successfully to demonstrate reproducibility of results consistent with the findings of other investigations, namely those reported for like compounds by the University of Dayton Research Institute in earlier work done by the TDAS and/or the TDU-GC system. The compounds studied for such comparison included the non-volatile pentachloronitrobenzene (solid) and the rather volatile chloroform (liquid).

However, the experience with heptane as a component in the feed to the TDU-GC suggests that there will be greater difficulty in properly assessing mixtures of organic compounds exposed to the thermal treatment process where one of the components in the feed is present in high concentration and thereby overshadows/masks the other components. For accurate measurement of effects of feed composition, great care must be exercised to limit mixtures to a very few, sometimes only two compounds that are individually "clean" in any GC analysis.

For more complete characterization of the thermal reactor emissions with respect to PICs formed in the thermal treatment process, more extensive procedures involving additional instrumentation is needed to identify and quantify PIC compounds. A Mass Selective Detector (MSD) dedicated to the TDU-GC system is the instrument of choice, both for accuracy of determinations and for volume of work that can be expedited. An alternative scheme for analyzing the emissions requires trapping the by-pass volume of effluent at the splitter ahead of the GC capillary column onto an adsorbent and then analyzing the adsorbed sample by an "external" Gas Chromatograph-Mass Spectrometer (GC-MS) unit to identify PIC compounds. This latter procedure offers the opportunity for identifying individual PIC compounds that otherwise might remain unknown. However, the various additional handling steps and transfer(s) of samples present a serious obstacle to accurate quantification. Practical limits to the load of samples that can be handled in this way would require great selectivity in the kind and number of samples that could be designated for analysis.

Thermal decomposition profiles (fraction of feed component remaining or observed in the emissions vs. temperature of thermal treatment) indicated the relatively refractory nature of such compounds as monochlorobenzene

and trichloroethylene and of Freon-113. The $T_{99.99}$ (2), temperature for 99.99% destruction of the feed component at 2.0 seconds residence time, for these three compounds were, by extrapolation of the thermal decomposition profiles, 850, 875, and 810°C, respectively.

The remarkable differences in PIC concentrations observed for chloroform under highly oxidative (ϕ of 0.05) and under reduced oxygen (ϕ of 0.76) atmospheres in the thermal reactor point out the impact of different conditions of the combustion process upon emissions that may occur in industrial operations. It appears that a temperature several hundred degrees (°C) higher is needed in a reduced oxygen atmosphere to obtain the same destruction level of PICs observed for the oxygen-rich atmosphere. Also, the generation/production levels of the PICs varied with the oxygen levels. Clearly, the mechanisms/rates for PIC formation were different in those different atmospheres. In the oxygen-rich atmosphere, there were no hydrogen-containing organic compounds detected in significant amounts (greater than one weight percent of the emissions) or identified (less than one percent). Also, the perchlorinated PIC compounds such as tetrachloroethylene and carbon tetrachloride were destroyed far more readily in the oxygen-rich atmosphere.

Early in the study, an experimental design treatment (9) through statistical evaluation of parametric projections and anticipated results was proffered as a means to streamline the investigative program. Unfortunately, various factors not able to be controlled and unknowns not anticipated at the time nullified this effort. Some of these were singularities of the "art" of performing the experimental runs that cannot be statistically accountable. For example, the use of a mini-injector syringe needed for some samples required a trial-and-error approach of timing the injection and of spotting the delivery tip at a certain depth in the insertion chamber, etc., in order to arrive at a consistent procedure for yielding acceptably reproducible results - this resolution before a planned series of runs at various temperatures might be considered. Another problem involved vapor samples of chloroform that yielded too small a quantity of the organic compound(s) in the emissions for satisfactory quantification of that less detector-sensitive compound; liquid samples were substituted for resolving that particular part of the study under the test conditions prevailing at that time. Of course, various equipment breakdowns not only stopped the course of investigation but even required back-tracking sometimes to re-establish a controlled set of operating conditions. The active interjection of various unknowns into the study procedure make experimental design ineffective in such a non-routine environment of investigation.

The emphasis of the study thus far has been on the exposure of individual hazardous waste compounds to high temperatures in a highly oxidative atmosphere. Low oxygen atmospheres, even pyrolysis conditions, should be investigated more thoroughly to get a true appraisal of the operating conditions responsible for the greater difficulty in destruction of organic compounds, namely the PICs.

In summary, the results of the TDU-GC work discussed here show that:

(1) Good reproducibility of results can be obtained from laboratory test systems of similar design

(2) Assessment of feed mixtures is a necessary but more difficult goal to obtain with the TDU-GC system as it is presently set up.

(3) There are differences in emissions from a reactor under reduced oxygen conditions and under rich oxygen conditions that can be quite large. They indicate the need for the more effective conditions of higher temperature and/or longer residence time in the incineration system to satisfactorily eliminate/reduce the products of emissions resulting from thermal treatment of hazardous waste compounds.

REFERENCES

1. Rubey, W.A., I.B. Fiscus and J.L. Torres. "Description of Operation of a Thermal Decomposition Unit-Gas Chromatographic System." University of Dayton Research Institute, Dayton, Ohio. U.S. EPA Cooperative Agreement CR-807815-01-0, 1982.

2. Graham, J.L., W.A. Rubey and B. Dellinger. "Determination of Thermal Decomposition Properties of Toxic Organic Substances." Presented at the 1982 Summer National Meeting of AIChE, Cleveland, Ohio, 1982.

3. Dellinger, B., D.S. Duvall, D.L. Hall, W.A. Rubey and R.A. Carnes. "Laboratory Determinations of High-Temperature Decomposition Behavior of Industrial Organic Materials." Presented at the 75th Annual Meeting of Air Pollution Control Association, New Orleans, LA, June 1982.

4. Rubey, W.A. "Design Considerations for a Thermal Decomposition Analytical System (TDAS)," EPA-600/2-80-098, U.S Environmental Protection Agency, Cincinnati, Ohio, August 1980.

5. Hall, D.L., W.A. Rubey and R.A. Carnes. "The Experimental Determination of Thermal Decomposition Properties of Toxic Organic Substances." Presented at Air Pollution Control Association Meeting on the Burning Issue of Disposing of Hazardous Wastes by Thermal Incineration, Newark, N.J., April 1982.

6. Rubey, W.A., J.L. Torres, D.L. Hall, J.L. Graham and B. Dellinger. "Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds." University of Dayton Research Institute, Dayton, Ohio. U.S. EPA Cooperative Agreement CR-807815-01-0, 1983.

7. Hall, D.L., J.L. Graham, N. Stamatiades and B. Dellinger. "The Thermal Decomposition Characteristics of Chloroform." Presented at the American Chemical Society Meeting, Chicago, Illinois, September 1985.

8. Staley, L.J., "Interim Report on Incinerator Operating Parameters Which Correlate with Performance." U.S. Environmental Protection Agency, Cincinnati, Ohio, September, 1985.

9. Show, I. "Statistical/Experimental Design Considerations for the Project: Non-Flame Hazardous Waste Thermal Destruction." Report from S-Cubed, LaJolla California to the EPA Hazardous Waste Engineering Research Laboratory, Cincinnati, Ohio, 1985.

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